Temperature dependent crystal and electronic structures of $CaCu_3Ti_4O_{12}$.

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A-site ordered perovskite $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much interest recently, because it shows a giant dielectric constant (ε~10^4) over a wide temperature range from about 100 to 600K and the dielectric constant decreases rapidly to one-hundredth without structural phase transition at the temperature under about 100K [1]. In this study, to clarify the origin of the dielectric anomalies, the electronic structure and local crystal structure were measured by means of X-ray Raman scattering (XRS) and X-ray fluorescence holography (XFH), respectively. XRS of TM $\underline{2p}3d$ and $\underline{2p}4d$ core-excitations (TM=Ti, Cu), where underlines denote a core-hole [2], and O 2*p* emission spectra were measured in hard and soft X-ray regions, respectively. The XRS showed increase of both Ti 3*d* and Cu 3*d*, and decrease of O 2*p* density-of-state with decreasing temperature, which suggests increase of covalency of both Ti-O and Cu-O.

A single crystal (100) sample of CCTO was used in this study. The XRS spectra were measured using X-ray emission spectrometer (ESCARGOT) at beamline BL-7C, Photon Factory, KEK. XFH experiment in the inverse mode was performed at beamline BL-6C. XFHs using each *Kα* fluorescence of Ca, Cu, and Ti was measured at room temperature, 120K and 80K.

Figure 1 shows Cu *K* XRS spectra measured at RT and 70K. The XRS shows decrease of the Cu 3*d* peak intensities at low temperature. Since the XRS reflects the unoccupied density-of-state, this result suggests the electron numbers in Cu 3*d* state increase at low temperature. In detailed temperature-dependent experiment, the Cu 3*d* peak decreased rapidly at about 100K that suggests the relation between electronic state and dielectric properties.

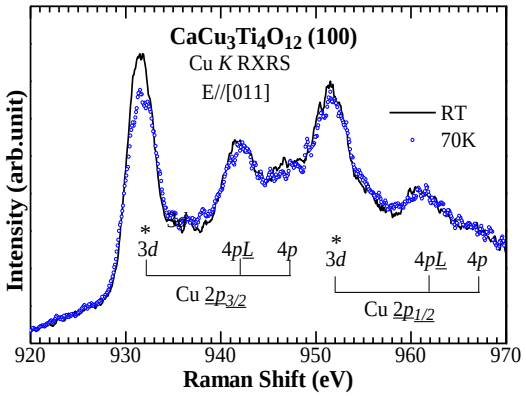

Fig. 1: Cu *K* XRS spectra: RT (line) and 70K (dot).

Figure 2 shows atomic images obtained from Cu *Kα* XFH experiment. Figs. 2(a) and 2(b) show images of nearest Ti layer from central Cu atom at RT and 80K, respectively. The circles are the position of the Ti-ion determined by XRD result, which reflects long range ordering. The atomic image of Ti-ion shows extra spots at RT (also at 120K), while the spots disappeared at 80K. The temperature dependence suggests the fluctuation of the Ti-ion would be the origin of the dielectric anomalies.

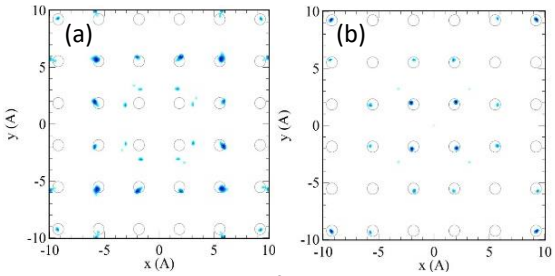

Fig. 2: Atomic Images of nearest Ti layer around central Cu atom obtained from Cu *Kα* XFH; (a) RT and (b) 80K.

References

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